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FACILE SYNTHESIS OF ALPHA-DEUTERATED ACRYLICS AND  
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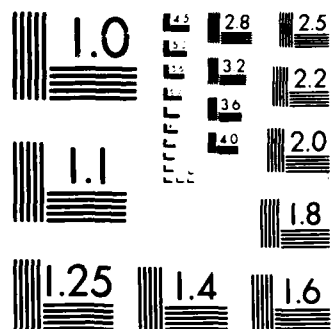
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Technical Report No. 4

FACILE SYNTHESIS OF  $\alpha$ -DEUTERATED ACRYLICS AND ACTIVATED VINYL

by

Lon J. Mathias and Ronald F. Colletti .

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A simple, direct exchange reaction has been discovered for vinyl groups in which the exchangeable deuterium of alcohols (e.g.  $\text{CH}_3\text{OD}$ ) or water ( $\text{D}_2\text{O}$ ) replaces only the  $\alpha$ -hydrogen of activated vinyls under catalysis by DABCO (1,4-diazabicyclo-[2.2.2]octane). Acrylate esters, acrylonitrile, and methyl vinyl ketone were found to undergo rapid exchange at room temperature to give easily isolated, pure and readily polymerizable  $\alpha$ -deuterated compounds. This procedure is the most general, efficient and cost-effective one available for obtaining such isotopically labeled materials.

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## Introduction

Enormous capability exists for studying reaction mechanisms, and the solution and solid state behavior of small molecules and polymers by  $^2\text{H}$  NMR. In polymer characterization, for example, the molecular relaxation times available using variable temperature wide-line techniques spans the range of characteristic frequencies from ca. 10 MHz to 1 Hz<sup>1</sup>. New methods of deuterium incorporation at pivotal positions are vital for expanded use of these techniques.

An additional advantage in using deuterated reactants in synthesis is that  $^2\text{H}$  NMR can be used directly to follow conversion, monitor intermediate formation and disappearance, and examine side-reactions and by-products. The present discovery stems from the combined use of  $^2\text{H}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  solution spectroscopy to monitor the synthesis of a deuterated monomer needed for another study<sup>2</sup>. The specific reaction under investigation involved functionalization of acrylate esters by reaction with aldehydes in the presence of DABCO<sup>3</sup>. In the absence of acceptor aldehydes, and in the presence of a suitable exchangeable deuterium donor, rapid incorporation of deuterium at the  $\alpha$  position was observed for a number of activated vinyl species (1 - 2). The Table summarizes our initial results.

TABLE

<u>compound</u>	<u>reaction conditions</u>	<u>% deuterium*</u>
methyl acrylate	30 min / CH <sub>3</sub> OD	93.7
butyl acrylate	30 min / CH <sub>3</sub> OD	81.8
acrylonitrile	30 min / CH <sub>3</sub> OD	90.5
"	10 min / D <sub>2</sub> O	82.0

\* determined by integration of the vinyl region of the <sup>1</sup>H NMR spectra.

We propose a DABCO-catalyzed equilibration (Figure 1) in which deuterium incorporation can be driven to high levels by use of a large excess of the deuterium donor. Levels of incorporation greater than 80% were obtained in minutes with a single exchange process. This procedure is straightforward in contrast to previously reported multistep methods of  $\alpha$ -deuteration of acrylates<sup>4,5,6</sup>.

While either CH<sub>3</sub>OD or D<sub>2</sub>O served in the exchange for acrylonitrile, hydrolysis of the intermediate species formed from acrylate esters occurred in D<sub>2</sub>O. In addition, higher alkyl esters underwent transesterification to methyl acrylate if the exchange reaction was extended. Exchange of methyl vinyl ketone was complete in a matter of minutes, although prolonged reaction led to Michael addition and aldol condensation products<sup>7</sup>.

The general procedure involves simply mixing together excess deuterium donor with the activated substrate, adding DABCO, and monitoring the reaction with <sup>1</sup>H or <sup>2</sup>H NMR. Figure 2 gives

representative spectra for methyl acrylate. The vinylic region of the  $^1\text{H}$  spectrum displays a typical ABX pattern with coupling constants  $J_{AB} = 1.5$ ,  $J_{AX} = 17.3$ , and  $J_{BX} = 10.2$  Hz. The deuterium spectrum displayed splitting of the  $\alpha$ - $^2\text{H}$  by the cis and trans hydrogens with  $J_{\text{D-H}_a} = 4.18$  and  $J_{\text{D-H}_b} = 2.52$  Hz. Complete  $^1\text{H}$ - $^2\text{H}$  equilibration was observed; eg, for methyl acrylate, 94% found vs. 92% theoretical.

These labeled materials, in addition to their value in forming specifically labeled polymers, should be useful in probing mechanisms in organic and natural product syntheses involving a variety of Grignard, Michael and Diels-Alder reactions.

#### ACKNOWLEDGEMENT

We gratefully acknowledge an instrumental grant from the Department of Defense through the Office of Naval Research for purchase of our Bruker MSL-200 NMR. This work was supported in part by the Office of Naval Research.



## LIST OF FIGURES

Figure 1. Equilibrium of DABCO intermediate.

Figure 2. a)  $^1\text{H}$  spectrum of undeuterated methyl acrylate, b)  $^1\text{H}$  spectrum of  $\alpha$ -d-methyl acrylate, and c)  $^2\text{H}$  spectrum of  $\alpha$ -d-methyl acrylate.

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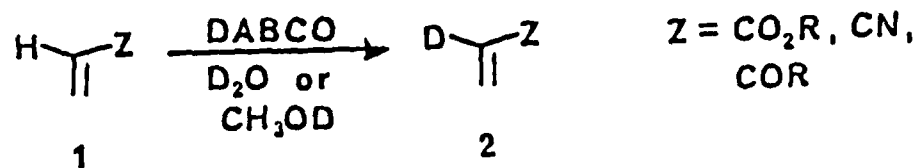


Figure 1.

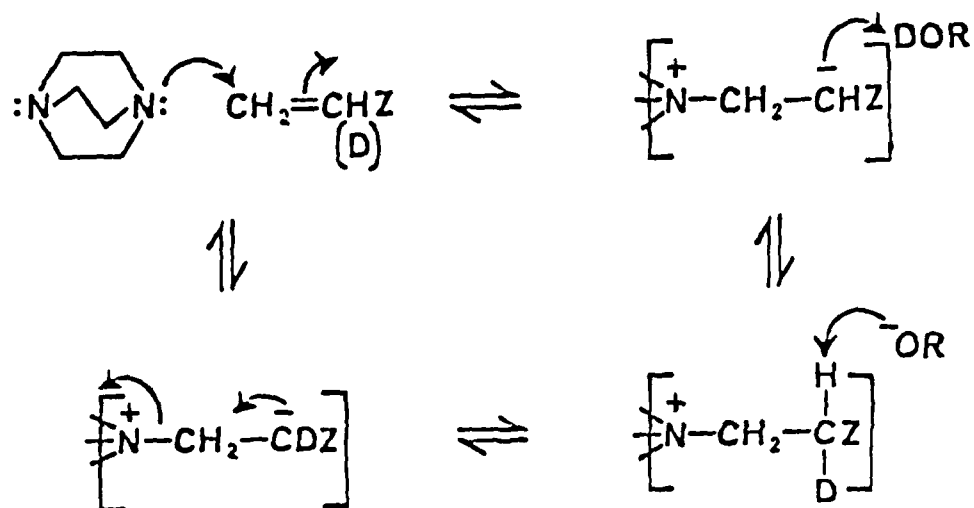
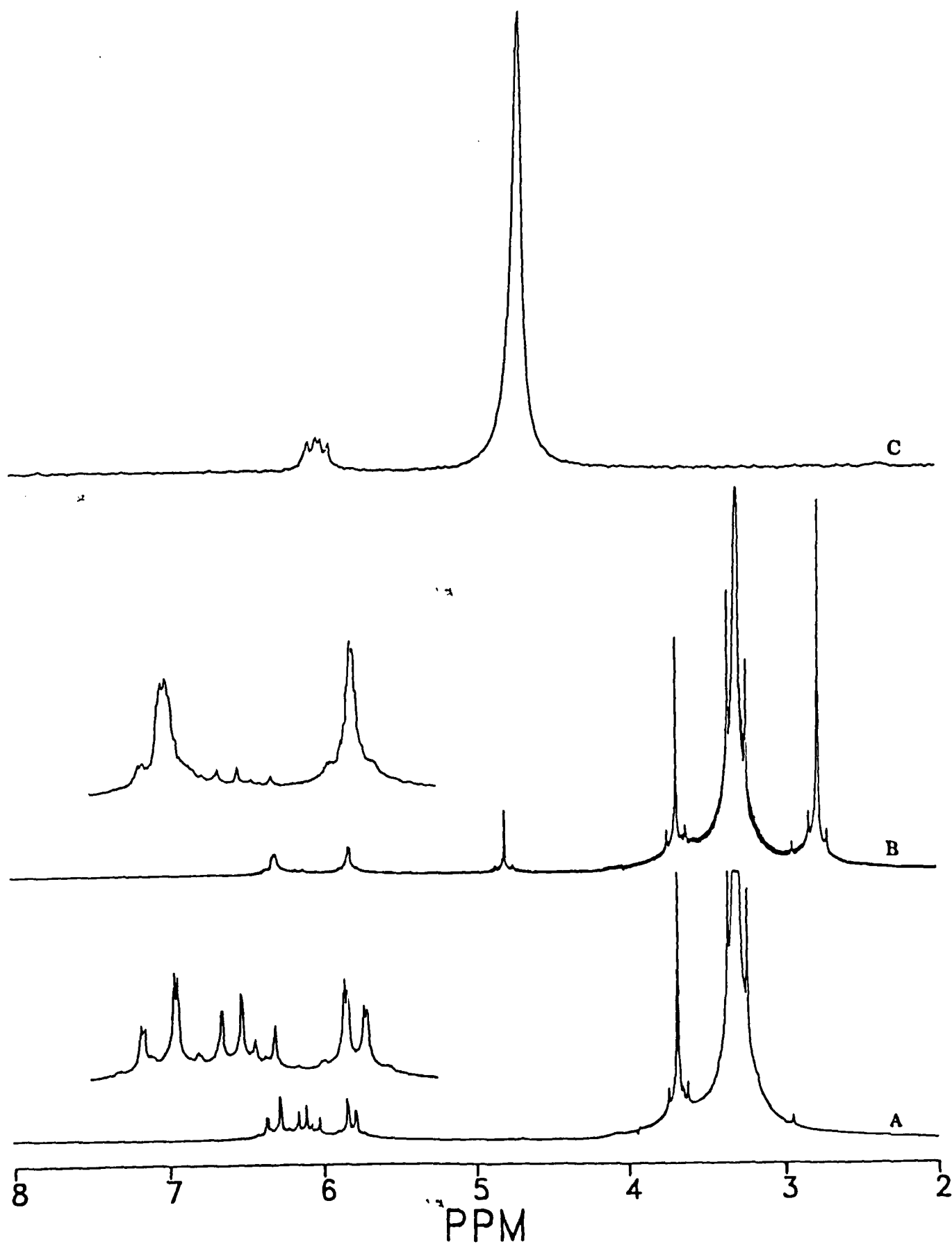


Figure 2.



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